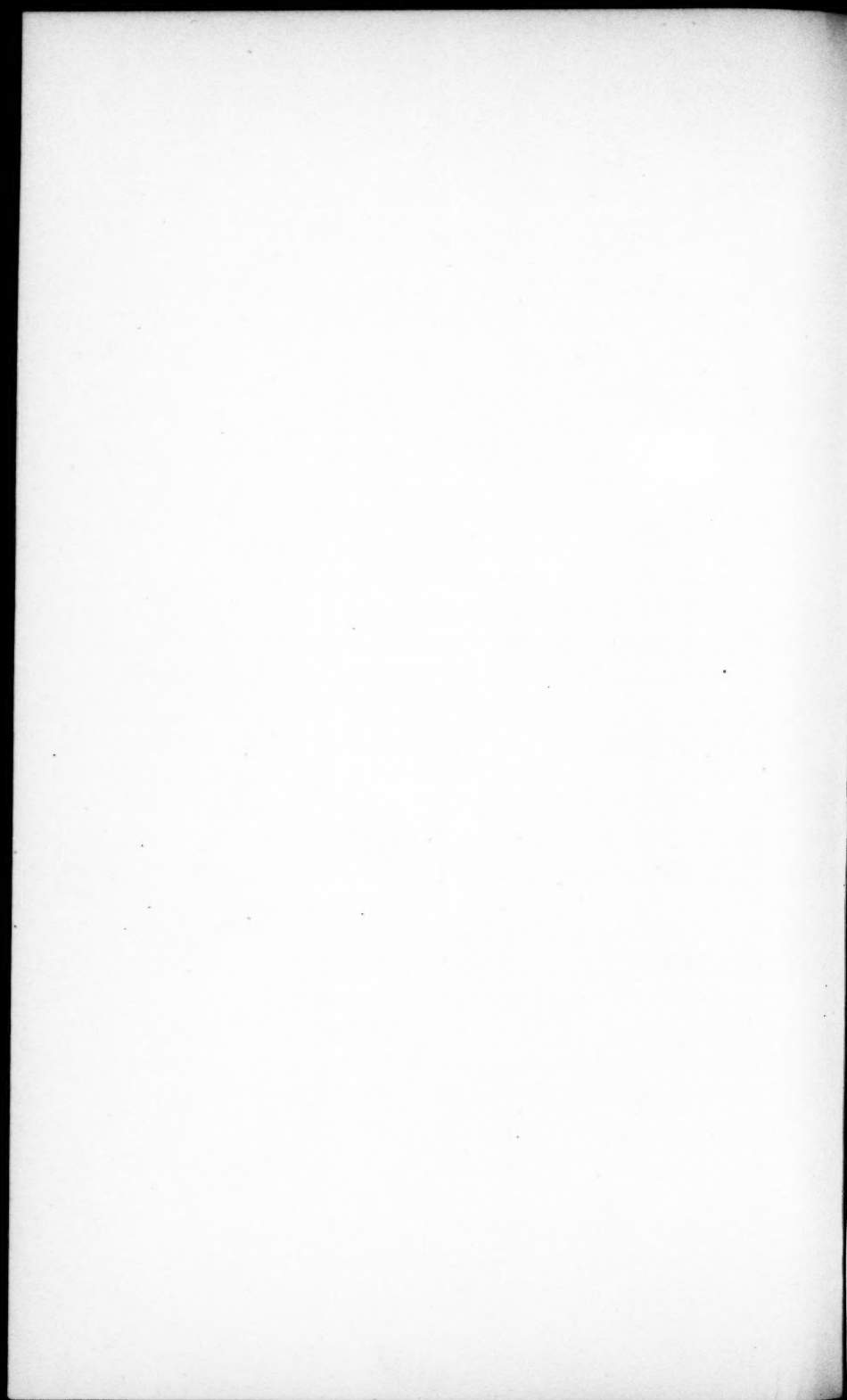CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
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CONCERNING THE ADIABATIC DETERMINATION OF THE HEATS OF COMBUSTION OF ORGANIC SUBSTANCES, ESPECIALLY SUGAR AND BENZOL.

BY THEODORE W. RICHARDS, LAWRENCE J. HENDERSON, AND
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Introduction.

As a preliminary step to the determination of the heats of combustion of an extended series of organic substances, desired for certain theoretical considerations, measurements were made on two common substances, cane-sugar and benzol. These substances were chosen in order that one might represent solids and the other volatile liquids, and because they may be easily obtained in a high state of purity, as well as because their heats of combustion have been carefully studied by other investigators.

This investigation offered the opportunity for further testing and improving the adiabatic calorimetric method recently proposed and tested by Richards, Henderson, and Forbes,[1] by means of which corrections for accidental loss of heat and for the lag of the thermometer are experimentally eliminated. The method was devised in the hope that its use might increase the accuracy of thermochemical work; and this hope is justified by the present experience. The principle of the method is to cause the temperature of the surroundings of the calorimeter to change in the same direction and at the same rate as the calorimeter itself. This is accomplished by surrounding the calorimeter with vessels in which a suitable warming reaction can take place in a manner fulfilling the above conditions. A reaction easily regulated and well suited to this purpose, namely, the neutralization of an alkali with an acid, was chosen for this purpose.

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[1] These Proceedings, **41**, 3 (1905); Zeit. phys. Chem., **52**, 551 (1905).

The Apparatus.

A vertical section of the apparatus is shown in the accompanying diagram. The large outer vessel (A) and the covering vessel (B), designed for holding the alkaline solution, were made of sheet copper. On account of the corrosive action of the caustic solution to which the vessels are continually exposed, the joints must be very thoroughly soldered, otherwise the corrosion may give rise to annoying leaks. These are of serious consequence if they occur in the cover, because then they may allow the solution to pass into the calorimeter or into the narrow air-space surrounding the calorimeter.

The inner vessel (C) protecting the calorimeter itself from the alkaline surrounding liquid was a heavy nickel-plated copper can well burnished in the interior and firmly adjusted in the outer vessel several inches above the bottom, so as to allow a free circulation of the liquid beneath it.

The calorimeter proper (D) was placed inside of this inner vessel, resting on several bits of cork and separated by an air-space of about two millimeters from its burnished nickel inner surface. This calorimeter was made of pure silver; it weighed 1357 grams and had a capacity of about 4432 milliliters; in operation it was filled with water, completely submerging the combustion bomb which rested upon points bearing on its base. The German-silver stirrer (E) which agitated the water in the silver calorimeter consisted of two perforated rings on upright supporting wires, and was moved up and down at a perfectly regular rate by means of an electric motor with a worm-gear attachment. This stirring arrangement was found to be very satisfactory, as it produced a complete and rapid adjustment of the temperature of the calorimetric system during a combustion, and the comparatively slow motion gave rise to no warming correction during the seven or eight minutes necessary for the actual combustion.

The copper pan (B) used as a cover to both calorimeter and outside jacket, was provided with copper tubes for the stirrers and thermometers projecting below it ; its temperature also was changed in the same manner as that of the outer jacket by adding acid to its alkaline contents, so as to follow the effect of the heat of the combustion. The liquid in the cover was stirred by a large oscillating perforated copper ring (F) actuated by the same motor which raised and lowered the stirrer of the calorimeter. It was found unnecessary to follow the change in temperature of the calorimeter as closely in the cover as in the jacket, although had this been necessary it might as easily have been done.

FIGURE 1.

Vertical Section.

A. Outer vessel.

B. Covering vessel.

C. Nickel-plated copper can.

D. Silver calorimeter.

E. Stirrer for calorimeter.

F. Stirrer for covering vessel.

H. Stirrer for outer vessel.

I. Copper cover.

J. Burettes.

K. Crucible containing substance to be burned.

L. Thermometer.
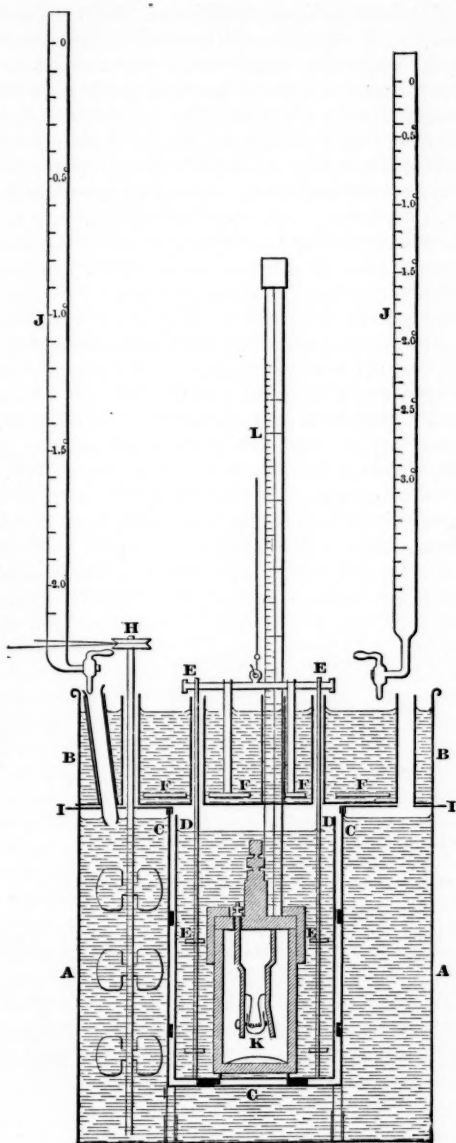
On the other hand, it is imperative that the heat generated by the reaction of the acid and the alkali in the outside can should be evenly and very quickly distributed, so that the change in temperature of the outer jacket may follow as closely as possible the change in temperature of the calorimeter. This was accomplished by running the acid into the alkaline solution in the immediate vicinity of a very powerful rotary stirrer (H), which drove the solution downward and at the same time around the vessel. This stirrer was propelled by an electric motor, and kept the liquid very thoroughly agitated. In order to prevent splashing into the calorimeter or into the air-space around the calorimeter, a covering sheet of copper (I) was bent down so as to fit snugly around the inner nickelled copper can (C); this sheet extended to the edge of the outer jacket. This cover effectually prevented injurious splashing, no matter how violent was the agitation of the liquid.

The acid was run both into the outer vessel and into the cover from burettes (J), which were calibrated, not in cubic centimeters, but in tenth degrees of temperature. In other words, the amount of acid necessary to raise each of the outer systems $\frac{1}{10}°$ was determined by trial, and the burettes were marked accordingly.

The bomb used in this work was made after the model of those used by Atwater by the firm of Dinsmore and Singleton, Middletown, Connecticut. The interior 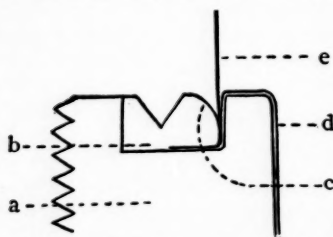and top of the bomb were lined heavily with platinum. Every part of the apparatus exposed to the oxygen under pressure during a combustion was of platinum, except a lead gasket which made the joint gas tight when the top of the bomb was screwed down. The presence of a rim of lead caused at first serious difficulty on account of its rapid oxidation by the oxygen under pressure during a combustion. This might introduce a small error of unknown and probably varying magnitude; in some cases the quantity of lead converted to oxide was considerable. Lead gaskets both gold-plated and covered with gold foil were tried without success. The difficulty was finally solved by the use of gold in the following manner. A lead gasket was fitted in position and the top screwed down upon it several times in order to form a depression in the centre

FIGURE 2. Detailed section of edge of bomb, a, showing the platinum lining, d, and the method of protecting the lead gasket, b, with gold foil, e. The gasket is partially cut away at c.

of the gasket and force out the sides. Some of the lead at the inner edge was then cut away as shown in the diagram. Small strips ☐ of sheet gold, previously annealed, were inserted around this edge so that they might overlap, after which the top was again screwed down several times in order to wedge in the strips of sheet gold. The gold was then bent back over the lead and the top screwed down in order to smooth out the gold lining. A lining of this sort proved entirely satisfactory, though in time a very slight oxidation of the lead occurred, due to the loosening of several of the gold strips. This oxidization was, however, too slight to affect the results, for when a new lining replaced the old, no variation in the results could be detected.

Instead of the shallow dish ordinarily used for holding the substance to be burned, a platinum crucible (K) weighing about 15 grams was substituted. The platinum crucible has probably several advantages over a shallow dish, especially in the combustion of liquids. The high sides of the crucible tend to prevent loss by projection of the material, and the heat at the moment of ignition is probably concentrated, thus securing a more complete combustion.

The thermometer (L) was made by Fuess after the ordinary Beckmann model, with a large bulb containing about 75 grams of mercury and possessing a wide and very freely moving thread of mercury. It had been standardized by the Prussian Physikalisch-Technische Reichsanstalt and was subsequently compared here with a most carefully constructed Baudin thermometer, and with another similarly standardized Beckmann thermometer. All measurements were made over about the same part of the scale, in order to make the results with benzol as closely comparable as possible to the results with sugar.

The oxygen used was similar to that used by Atwater, and was obtained already compressed in steel cylinders from the White Dental Company of Boston. In order to insure a certain standard of purity in the oxygen, samples of each cylinder were analyzed volumetrically for oxygen, and check combustions were frequently performed with sugar. As a rule, this oxygen contained between 2.7 and 3.2 per cent of nitrogen and no chlorine. In work at present in prospect, it is proposed to prepare purer samples of the gas. The effect of the impurity of nitrogen is discussed in detail below.

PURIFICATION OF MATERIAL.

Cane-Sugar, $C_{12}H_{22}O_{11}$. Three samples of sugar, designated A, B, and C, were used in this investigation. The source of each sample was the crystallized sugar or "rock-candy" of commerce. For the first, called Sample A, powdered "rock-candy" was dissolved in boil-

ing distilled water until the solution was almost saturated.   The hot solution was filtered through asbestos in a platinum Gooch crucible and allowed to cool in low crystallizing dishes.   After inoculating the solution with several minute sugar crystals, the substance began to crystallize slowly in fine granular crystals.   Several days afterwards the sugar was separated from the syrup by filtration through a Gooch crucible with suction, being washed with distilled water several times during the process.   When the greater part of the solution had been drawn off, the sugar was put into short funnels fitted with platinum cones and subjected to centrifugal action.   During the whirling it was several times washed and stirred with distilled water.   The sample was desiccated, powdered in an agate mortar, and preserved in a desiccator.

Because this sample, A, might be not completely free from included water, another sample of sugar was crystallized from its solution in a mixture of water and ethyl alcohol which had per gram the same heat of combustion as sugar.   In this case, if the sugar included some of the liquid from which it was crystallized, the weighed mother-liquor would give the same heat of combustion as an equal weight of sugar.   This preparation was conducted in the following way.   A concentrated solution was made from powdered "rock-candy" and a known quantity of hot distilled water ; and while the solution was still hot, it was filtered through asbestos in a platinum Gooch crucible.   To this solution was added such a weight of absolute alcohol that the mixture of water and alcohol should have the same heat of combustion as sugar.   After standing a short time, the sugar began to separate out as fine granular crystals.   The dishes with the sugar solution were covered, and at the end of several days the sugar was filtered off and treated in the same manner as sample A, except that it was washed with a mixture of water and alcohol having the same heat of combustion as sugar.

The third sample, C, was prepared at a different time and with different material, but in a manner similar to the latter method.

Benzol, C_6H_6.   Two samples of benzol were prepared as follows. For the first, sample A, 500 grams of Merck's benzol, freed from thiophene, were agitated in a flask submerged in a bath of ice and water until about two thirds had crystallized.   The crystals were allowed to drain slowly, so that any adhering benzol might be washed off by the liquid formed from the melting crystals.   The crystals were then allowed to melt and the above process repeated three more times.

For the second, sample B, the same quantity of Kahlbaum's similar preparation was agitated in a flask submerged in a bath of ice and water until about one third of the benzol had crystallized.   These crys-

tals were drained, melted, and then recrystallized, about the first fifth of the crystals being discarded.   From the remaining benzol about one third was allowed to crystallize.   These crystals were drained, melted, and recrystallized as before, the first crystals being discarded.   About one half of the remaining benzol was allowed to crystallize and was retained as the final sample.   The freezing-point of this sample was determined in a regular Beckmann freezing-point apparatus, using all of the precautions to prevent supercooling.   The freezing-point was found to remain constant until practically all of the sample tested was frozen, thus indicating its purity.   Especial care was taken to keep these preparations free from dust and other impurities, both during and after the purification.

The thermochemical results showed that these two samples were essentially the same, as far as the present purpose was concerned.

THE COMBUSTION OF SUGAR.

The details of conducting a combustion of sugar in the calorimetric bomb in the adiabatic calorimeter are easily told.

About 1.5 grams of sugar were accurately weighed in the platinum crucible in which the substance to be burned was placed.   The sugar was not compressed into tablets, as has been the custom of previous investigators, but was burned as a powder.   This method is the less troublesome and also the safer one, in that it involves less manipulation of the substance ; moreover, in a preliminary series of experiments it was found that powdered sugar and sugar tablets gave perfectly concordant results.

The platinum crucible was placed in its support, a platinum ring secured to one of two stout platinum wires projecting downward from the cover of the bomb.   These wires formed the terminals of an electric circuit.   A spiral of very fine iron wire to serve as the igniter was suspended between them, dipping into the crucible and buried in the sugar.   A small amount of water, never more than a milliliter, was sprayed into the bomb, so that the space might be saturated with water-vapor, in order to avoid a correction for the evaporation of part of the water formed by the combustion.   The cover was then placed on the bomb, and a gas-tight joint was made by means of the screwcap fitting over it.   Oxygen was run into the bomb until it was under a pressure of 35 atmospheres.   This high pressure was always used, in order to be more certain of obtaining complete combustion, unless otherwise indicated.

Meanwhile the rest of the apparatus was being prepared.   The dilute alkaline solution in the jacket and cover was brought to a temperature

a little below that of the room, and the bomb was placed in the silver calorimeter.   Connections were prepared for the later use of an electric current by joining a copper wire to the bomb itself, and another, carefully insulated, to the tip of that one of the two stout platinum wires which was insulated from the bomb.   The water for the calorimeter, 3302 grams at 20° C., was now measured in a marked flask, and poured into the silver vessel, submerging the bomb, at nearly the temperature desired. The cover containing dilute alkali was put in position, and its temperature roughly adjusted to that of the calorimeter.   The stirrers were set in motion, and the thermometers and burettes clamped in position.   The temperatures of the two systems were taken with a 0.01° thermometer ; if, after all was ready, a slight difference existed between the temperatures of the calorimeter and the other jackets, the latter were easily adjusted by a little ice, or a little hot water or acid, until the whole apparatus was very nearly the same temperature throughout, that is to say, within a few hundredths of a degree.   All measurements were made between 20° and 25° C.   Readings every one or two minutes were now taken on the accurate Fuess thermometer, which was always jarred by an electric vibrator before reading, in order to prevent errors due to friction of the mercury thread.   As soon as the readings assured constancy of the temperature of the calorimeter, the switch, completing the electric circuit through iron wire in the bomb, was lowered, and the sugar ignited by the combustion of the wire.[2]   In a few seconds the temperature of the calorimeter began to rise, and the change in temperature was equalled in the outer system by adding concentrated sulphuric acid from the burettes.   For about the first minute the temperature of the outer system, as indicated by the quantity of sulphuric acid used from the burettes, was kept about 0.1° to 0.05° above that indicated by the thermometer in the calorimeter, so as to allow for thermometric lag and give time for the equal distribution of the heat in the jacket.   In from four to five minutes the calorimeter reached its maximum temperature, and the thermometer gave constant readings.

The great advantage of this adiabatic method of calorimetry is shown at this point by the constancy of the thermometer at the completion of the combustion.   The thermometer usually gave constant readings for a long time after it had reached its maximum, showing indubitably that there was no appreciable heat exchange between the calorimeter and its surroundings.   Moreover, there was plenty of time in which to read the thermometer accurately, while the mercury thread was stationary, and no thermometric lag was possible.

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[2] The electrical heat thus introduced is very small in amount, and is wholly eliminated by the comparative method finally used for calculating the results.

After the combustion, the pressure of the gas in the bomb was relieved and the bomb opened. The interior of the bomb and the crucible were always inspected for any caramel or unburned sugar, but in only two cases among the preliminary and rejected experiments was any trace of caramel noted. The remaining gas was repeatedly analyzed after combustions of sugar for carbon monoxide, with negative results. Any unburned iron wire was measured, and a correction subtracted from the known heat of combustion for the original amount used. The interior of the bomb and the crucible were rinsed with distilled water, and these washings, containing the nitric acid formed in the combustion, were titrated with a solution of sodium hydroxide, which was standardized so that one milliliter was equivalent to a known rise in temperature of the calorimetric system. Corrections for the burning of the iron wire and the formation of nitric acid were of course subtracted from the observed rise in temperature.

The data of a typical combustion of cane-sugar follow.

Combustion No. 2.

The weight of sugar (Sample A) taken was 1.5270 grams. The calorimeter was adjusted at 2.55 o'clock.

Time.	Reading of thermometer in calorimeter.	
3.03	1.495°	Temperature of jacket = 1.50°
.05	1.496	Temperature of cover = 1.50
.06	1.496	
.07	1.496	
.08	1.496	

The sugar was ignited at 3.08.10 o'clock, and the rapidly rising temperature of the interior was equalled in the jackets and cover.

Time.	Reading of thermometer in calorimeter.	
3.10	3.050°	
.11	3.108	
.12	3.116	
.13	3.117	Temperature of jacket = 3.11°
.14	3.117	Temperature of cover = 3.19
.15	3.117	
.17	3.117	
.18	3.117	

The observed rise of temperature was therefore
$$3.117° - 1.496° = 1.621°.$$

15 cm. iron wire were burned, causing a correction of   —0.015°
4.1 milliliters of sodium hydrate solution were used, indicating
     nitric acid corresponding to a correction of   —0.003°
The correction for graduation of the thermometer was   +0.001°

<div align="right">Total,   —0.017°</div>

Therefore the corrected rise of temperature is

$$1.621° - 0.017° = 1.604°.$$

This would correspond to 1.050° per 1 gram cane-sugar.

Below is given a table containing all the results with sugar, except the few rejected preliminary determinations.

DATA CONCERNING THE COMBUSTION OF SUGAR.

Number.	Sample.	Rise in Temperature per gm. Cane-sugar.	Average.
1	A	1.050 ? *	°
2	A	1.050 *	1.0506
3	A	1.052 *	
4	B	1.050	
5	B	1.050	
6	B	1.051	
7	B	1.050	1.0504
8	B	1.050	
9	B	1.052	
10	B	1.050	
11	C	1.049 †	
12	C	1.052 †	1.0503
13	C	1.050 †	
14	C	1.050 †	

Average of 14 determinations, 1.0504°.

* Under a pressure of 25–27 atmospheres of oxygen.

† Combustions made by L. J. Henderson. All others were made by H. L. Frevert.

The purity of the sugar is indicated by the essential identity of the results obtained from three different samples.

In Determinations Nos. 7 and 8 the bomb was exhausted before running in the oxygen, and in Determinations Nos. 9 and 10 the amount of nitrogen was increased to about 13 per cent by volume in the compressed atmosphere of the bomb, by pumping in air in the first place, and then supplying the oxygen to 35 atmospheres pressure. The essential identity of these results with the others shows that the presence of even this large amount of inert gas does not affect the heat of combustion of a substance so easily burned as sugar.

In these experiments it appears probable that the greatest experimental error in a combustion lay in the reading of the thermometer. Probably with a scale divided to $\frac{1}{100}°$, even with a good lens, one may make an error of $0.001°$. Should this error be made in the same direction in the two extreme readings, the errors would cancel each other. However, should the errors be made in opposite directions, then in a rise of two degrees this error in reading the thermometer would amount to a percentage error of 0.1 per cent. The average result should be much more accurate than this, however. The agreement of the results of cane-sugar is in accord with this consideration of error. In the future, measurements of the more important substances, when other conditions justify a greater refinement, will be made with a platinum resistance thermometer.

THE COMBUSTION OF BENZOL.

The first problem to be solved in the combustion of a volatile liquid was to devise a method by which an accurately weighed quantity of it might be burned. Berthelot [3] determined the heat of combustion of benzol by saturating cellulose with the liquid, which was then ignited in the bomb. This method of procedure is evidently open to the error of a varying loss in weight of benzol by evaporation. Besides, since in this case some of the benzol must burn as vapor, which of course gives a greater heat of combustion than liquid benzol, a correction should be subtracted accounting for the heat of evaporization of that portion of the benzol burned as vapor. These objections account, in part at least, for the irregularity of his results.

Julius Thomsen [4] burned benzol both as vapor mixed with air and as a liquid in his Universal Burner. By these methods he obtained at various times four series of results, one of which was not at all in

[3] Ann. Chim. et Phys. (5) **23**, 193 (1881).
[4] Thermo. Untersuch., **4**, 59.

agreement with the others.   Probably, as Stohmann pointed out, the results with the Universal Burner were too high.

Stohmann [5] obtained most of his values for benzol by combustion in a different kind of lamp.   Subsequently,[6] however, he sealed benzol in very thin glass bulbs which were placed in the bomb and broken by shaking just before the bomb was placed in the calorimeter.   This method involved a necessary correction for the benzol burned as vapor. Stohmann thus secured two results concordant with those previously obtained, but he had much difficulty on account of the incomplete combustion of the benzol.   Of a series of determinations, he obtained only these two which were not vitiated by the deposition of soot on the interior of the bomb.

In order to burn completely a weighed quantity of liquid benzol without applying a correction for vaporization, the following procedure was followed in the present investigation.   Thin glass bulbs of about 0.7–0.8 milliliters with bent capillary stems were weighed, and filled with benzol by immersing the stems under benzol, alternately cooling and warming the bulbs in cold and hot water.   The thin walled capillary stems, filled with benzol, were sealed off near the bulbs in a fine blowpipe flame.   In this way bulbs could be obtained either completely filled or with a negligible amount of vapor in the short capillary stem.[7]   The bulbs and the detached capillary stems were weighed together under the same conditions as the empty bulbs, and the weights of benzol thus determined.

For combustion one of these bulbs was placed upon the top of about 0.25 gram of carefully weighed pure sugar in the combustion crucible, and the rest of the procedure was exactly the same as in the case of cane-sugar.   The great heat of the burning sugar caused the bulb of benzol to burst with the consequent immediate combustion of the benzol.   In the preliminary trials small patches of soot due to incomplete combustion of the benzol were noticed on the crucible and on the lining of the bomb.   This inadmissible complication was traced to the fact that the stems of the bulbs were from one to two centimeters in length.   After sealing new bulbs in such a way that the stems were only three to five millimeters long, no trace of soot ever appeared. Some idea of the temperature in the crucible at the moment of combustion may be gained from the fact that after a combustion the glass

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[5] Jour. f. prak. Chem., **33**, 241 (1886).

[6] Ibid., **40**, 77 (1889).

[7] This method of enclosing liquids in thin bulbs in such a way as to be capable of subjection to high pressure was first used by Richards and Stull in their work on Compressibility (Carnegie Inst. Pub., 7, 1903).

of the bulbs was always found at the bottom of the crucible fused into small globules.

A peculiar nitrous odor was in some cases observed in the gas in the bomb after a combustion. In order to discover whether this odor might be due to the formation of small amounts of some of the oxides of nitrogen which were not completely absorbed by the water, the following test was made on the gas in the bomb after combustions No. 12 and No. 25. The gas from the bomb was allowed to bubble slowly through gas-washers made of test tubes containing cold distilled water. This water was then boiled for some minutes to expel carbon dioxide, and was then titrated with a very dilute sodium hydroxide solution and phenolphthalein. The first drop of alkali turned the solution red, so there must have been very little of the acid-forming oxides of nitrogen, nitric or nitrous acids in the gas. Any nitric oxide formed in the bomb would have been immediately converted to nitrogen peroxide in presence of the excess of oxygen, and would have dissolved in the water. The washings of the bomb also were tested for nitrous acid with α-naphthylamine and sulphanilic acid; but negative results only were obtained. In a number of other determinations under varying conditions (Nos. 21, 22, 23, 24, 27), no odor whatever was noticeable in the escaping gas, although the quantitative results were not essentially different from similar ones in which an odor was noticed. Hence it appears that whatever may have caused this odor, it has no appreciable effect on the heat of combustion of benzol; no connection could be found between the presence of the odor and the effect of increasing the per cent of nitrogen present. Nevertheless the matter will receive further attention in the future.

The first trials of this method were from one cause or another unsuccessful, as is usual in such cases; but after eleven such partial failures satisfactory results were regularly obtained. After a series of five consistent values (Nos. 12–16) for benzol had been found, two combustions (No. 17 and No. 18) were made in which the air in the bomb was almost entirely removed before the oxygen was run in. It was hoped that two advantages might be gained by conducting the combustion in the absence of the nitrogen of the air originally contained in the bomb : first, that the cause of the nitrous odor might be removed; second, that the correction for the formation of nitric acid would be decreased. These new experiments gave for the heat of combustion of benzol a value higher than the average previously obtained by over 0.3 per cent, — a greater deviation than could be ascribed to the errors of the method. This interesting observation being new, so far as we could discover, the matter was pursued further. Three more combustions

(Nos. 19, 20, and 21) were made in the usual way with the bomb origi-
nally filled with air, and the average value for the heat of combustion
of benzol in this series was the same as that obtained in the first series.
Again three combustions (Nos. 22, 23, and 28) were made with the air
removed from the bomb before the oxygen was run in, and again results
were obtained more than 0.3 per cent greater than the results of the
combustions in which the bomb was filled with air at the beginning.
At the same time, in those cases in which the bomb was exhausted
the amount of nitric acid formed during a combustion did not appreci-
ably diminish, hence it was evident that the oxygen in use must
contain nitrogen.

After due consideration of these results the logical conclusion seemed
to be that the presence of an inert gas such as nitrogen in some way
or other interfered with the complete burning of the benzol, and there-
fore lowered the heat of combustion. In order to test this hypothesis
further, more combustions were made in the presence of still greater
concentrations of nitrogen, under which conditions the heat of com-
bustion should be still more diminished. To accomplish this, air was
forced into the bomb by means of an ordinary bicycle-pump, and the
pressure of the air forced in was measured on the pressure-gauge.
Oxygen was then run in until the pressure inside the bomb was 35
atmospheres. Since the amount of nitrogen in the oxygen had been
determined, it was a simple matter to calculate the approximate
amount of nitrogen in the bomb. The results of the combustions
made under these conditions agreed with the hypothesis, and while
the relation was not a simple ratio, yet the results showed clearly
beyond a doubt that the greater the concentration of nitrogen the
lower the heat of combustion. This effect of nitrogen in combustion
suggests the retarding influence of oxygen on the rate of formation
of hydrochloric acid when hydrogen and chlorine are exposed to the
light,[8] and numerous similar phenomena, sometimes classified under
the general head of negative catalysis.

In presenting these results, a typical determination is given in detail,
in order to illustrate further the method of calorimetry; afterwards a
table giving all the later results with benzol is recorded.

Determination No. 23,

Weight of benzol (A), 0.5840 gram.

Weight of sugar (B), 0.2073 gram.

Air was exhausted from the bomb before admitting oxygen.

The bomb was immersed in the calorimeter at 11.25 o'clock, and
the temperature of jacket and cover were adjusted at 11.30 o'clock.

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[8] Bunsen and Roscoe, Pogg. Ann., 96 (1855); Phil. Trans., **147**, 389 (1857)

Time.	Reading of thermometer.	
11.33	2.326°	Temperature of jacket = 2.31°
.35	- 2.327	Temperature of cover = 2.32°
.37	2.328	
.39	2.330	
.41	2.330	
.43	2.330	
.45	2.330	

Ignition occurred at 11.45.

Time.	Reading of thermometer.	
11.47	4.07°	
.48	4.110	
.49	4.116	
.50	4.117 +	
.51	4.118	
.52	4.118	
.53	4.118	Temperature of jacket = 4.10°
.54	4.118	Temperature of cover = 4.20°

Observed rise of temperature = 4.118° − 2.330° = 1.788°

There was little if any odor in gas remaining in the bomb after combustion.   11.0 centimeters of iron wire were burned, and 4.0 milliliters of the solution of sodium hydrate were used.

From the observed rise of temperature, 1.788°, the following corrections must be subtracted :

For error in graduation of thermometer =				−0.001°
For the combustion of 0.2073 gram sugar =				−0.218°
" " " " 11 cm. iron wire =				−0.011°
" " " " nitrogen to nitric acid =				−0.003°
			Total,	−0.233°

Therefore the combustion of 0.5840 gram of benzol raises the temperature 1.788° − 0.233° = 1.555°, and 1 gram of benzol would raise the temperature 2.662°.

In this result, 2.662°, mistakes of 0.001° in reading the initial and final thermometric height would cause an error of almost 0.004°, if the mistakes happened to be in opposite directions.   On comparing a number of determinations, one would therefore expect to find an occasional deviation from the mean as large as this ; but the mean should be much more accurate, because in many determinations such accidents tend to

balance one another.   The study of the results given below confirms
these inferences.   The following table is arranged according to the
amount of nitrogen present in the oxygen at the time of burning;
it contains the results of all the combustions except the rejected
preliminary ones.

Determination No.	Sample of Benzol.	Per cent Nitrogen.	Rise in Temperature of System for 1 gm. Benzol.	Average and Probable Error.
23	A	2.7	2.662°	2.662° ±0.0006
28	A	3.2	2.661	
17	B	2.7	2.661	
18	B	2.7	2.663	
22	B	2.7	2.663	
12	A	4.9	2.655	2.655 ±0.0007
13	A	4.9	2.658	
14	A	4.9	2.653	
15	A	4.9	2.656	
16	B	4.9	2.651	
19	B	4.9	2.657	
20	B	4.9	2.657	
21	B	4.9	2.650	
26	A	9.7	2.660	2.650 ±0.0023
25	B	9.6	2.649	
24	A	10.1	2.643	
27	B	11.9	2.650	

It is seen at once, from the averages in the right-hand column, that
an increasing amount of nitrogen decreases the heat of combustion
to an extent far beyond the limit of accidental error.   In this respect
the results with benzol are very different from those with sugar, which
has previously been shown to be unaffected by the presence of much
nitrogen.   The nature of the gaseous or liquid unburnt residue in the

case of benzol has not been determined; solid carbon, at least, was wholly absent.

Those determinations in which the least nitrogen was present undoubtedly represent the closest approach to the true value for the heat of combustion of benzol.   The first average of five determinations in the presence of about 3 per cent of nitrogen gives 2.662° as the rise in the calorimetric system for 1 gram of benzol.   This, in our opinion, represents a minimum value; the true one may be yet higher. It is planned to determine soon the heat of combustion of benzol in the presence of pure oxygen.

Obviously, data on only two substances will not permit the drawing of certain general conclusions.   Nevertheless, it seems reasonably probable that the effect in general of the presence of an inert gas during the combustion of easily burned substances is very slight.   On the other hand, other substances like benzol which need much oxygen for their combustion are probably, like it, affected by the presence of an inert gas.

Since the water-equivalent of our bomb and calorimeter has not been determined either by the method of finding the sum of the water-equivalents of the component parts, or by the admirable electrical method of Jaeger and von Steinwehr,[9] absolute values for the heats of combustion of sugar and benzol cannot be computed from these data.   Until an accurate value for the absolute heat of combustion of some standard pure substance has been obtained, the present results may be expressed as ratios, taking the rise in temperature of the calorimetric system caused by the combustion of one gram of cane-sugar as the standard of reference.   Such ratios can be easily converted to absolute values when a standard has been established, and moreover, the relative values can be used to the same purpose as absolute values in the application of heats of combustion to the primary idea which instigated the present work.   The outcome of the present work is thus that a gram of benzol yields at least $\dfrac{2.662}{1.0504} = 2.5342$ times as much heat on combustion as a gram of sugar.

It is interesting to compare this result with the results of other experimenters.   On account of the relation which exists between the weight of water and the weight of metal in the bomb-calorimetric system, and the fact that at temperatures between 0°–30° the specific heat of water decreases, while the specific heats of the metallic parts of

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[9] Verhandl. d. d. physik. Ges., **5**, 60 (1903); Ibid., **5**, 353 (1903); Zeit. phys. Chem., **53**, 153 (1905).

the calorimetric system increase with rise in temperature, the water-equivalent of the calorimetric system varies but slightly with change in temperature. In fact, the roughly calculated water-equivalent of our calorimetric system at 20° varied from its water-equivalent at 25° by less than 0.03 per cent. The estimated water-equivalents used in this comparison were, of course, not accurate, but the ratio between them must be very close to the truth. On the assumption that the relation between the weights of the water and the metallic parts in the calorimetric system of other investigators did not differ much from ours, it is evident that but little error will arise in comparing our results obtained at an average temperature of 21.4° with the results of Stohmann and of Fischer at average temperatures of 17° and 15° respectively.

The results of previous investigators, expressed both in gram-calories and kilojoules, are tabulated below.

RESULTS OF OTHER EXPERIMENTERS.

	Cane-Sugar.		Benzol.	
	Calories per Gram at Constant Volume and Pressure.	Kilojoules per Gram at Constant Volume and Pressure at 21°.	Calories per Gram at Constant Volume.	Kilojoules per Gram at Constant Volume at 21°.
Stohmann [10] . .	3955.2	16.533	9977	41.704
Fischer and Wrede [11]	3977.8	16.627	. . .	. . .
Berthelot [12] . .	3961.7	16.560	9949	41.587

Thus our ratio for the heats of combustion of benzol and sugar, 2.534, is about 0.3 per cent higher than 2.527, Stohmann's corresponding ratio. It is interesting to note that had we used the value for benzol obtained when the bomb was filled with air at the beginning, our ratio would have been $\frac{2.655}{1.0504} = 2.528$, which is practically the same as Stohmann's.

[10] Stohmann and Langbein, Jour. prak. Chem., **45**, 313 (1892); **40**, 77, 81 (1889); Stohmann, Rodatz, and Herzberg, ibid., **33**, 193 (1886).

[11] Sitzb. Berl. Akad. d. Wissen, **19**, **20**, **21**, 687 (1904). Value corrected for error in calibration of bomb, vide, Zeit. phys. Chem., **53**, 164 (1905).

[12] Berthelot and Vielle, Ann. Chim. Phys. (6), **10**, 442 and 458 (1887). Berthelot, Ann. Chim. Phys. (5), **23**, 193 (1881).

The very wide difference between the absolute heats of combustion of sugar as given by Stohmann and Fischer makes a calculation of the absolute value for benzol from the combination of our results with either of theirs a somewhat uncertain matter.   If Stohmann's value for sugar be accepted, 41.89 kilojoules is computed as the heat of combustion of a gram of benzol ; but if Fischer's be accepted, 42.13 kilojoules must be taken as the true value.   No attempt will be made in the present paper to decide this discrepancy, which is probably due either to different standards of temperature or to different standards of heat capacity in the two cases.

In conclusion, it is a pleasure to express our indebtedness to the Rumford Fund of the American Academy of Arts and Sciences for pecuniary support at the commencement of these experiments, and to the Carnegie Institution of Washington for further assistance during their continuation.

SUMMARY.

1. The adiabatic method of calorimetry devised by Richards, Henderson, and Forbes, as applied to the determination of heats of combustion with the calorimetric bomb, was improved and thoroughly tested.

2. The efficiency of this method in eliminating all corrections for heat exchange with the surroundings, and for thermometric lag, was established.

3. A new method was devised for burning an accurately weighed quantity of a liquid in the calorimetric bomb, by sealing it in a thin completely filled bulb, and exploding this by the combustion of a small amount of sugar.

4. The effect of an inert gas, nitrogen, on the heat of combustion of substances was noted for the first time.

5. In the calorimetric combustion of substances needing much oxygen it was shown that the presence of nitrogen may involve a very considerable error.

6. Benzol was found to evolve at least 2.534 times as much heat as an equal weight of sugar on burning.

EXPERIMENTAL DATA—TABLE I.

SUGAR.

Sample.	Number of Combustion.	Weight of Sugar.	Initial Temperature.	Final Temperature.	Observed Rise in Temperature.	Thermometer Correction.	Correction for Iron Burned.[1]	Correction for HNO₃ formed.[2]	Corrected Rise in Temperature.	Rise in Temperature per Gram Sugar.
		gms.								
A	1	1.4985	1.240	2.830 (?)	1.590	+0.001	−0.015	−0.003	1.573	1.050 (?)
A	2	1.5270	1.496	3.117	1.621	+0.001	−0.015	−0.003	1.604	1.050
A	3	1.5019	1.686	3.281	1.595	+0.001	−0.018	−0.003	1.580	1.052
B	4	1.5125	1.421	3.026	1.605	+0.001	−0.015	−0.003	1.588	1.050
B	5	1.5211	1.826	3.441	1.615	0.000	−0.015	−0.003	1.597	1.050
B	6	1.6705	2.916	4.693	1.777	−0.003	−0.014	−0.004	1.756	1.051
B	7	1.4137	2.010	3.511	1.501	+0.001	−0.015	−0.002	1.485	1.050
B	8	1.4957	1.464	3.051	1.587	+0.001	−0.014	−0.003	1.571	1.050
B	9	1.5486	1.323	2.969	1.646	+0.001	−0.012	−0.005	1.630	1.052
B	10	1.5402	1.248	2.883	1.635	−0.001	−0.014	−0.004	1.618	1.050
C	11	1.7317	1.023	2.859	1.836	−0.001	−0.015	−0.008	1.817	1.049
C	12	1.5586	1.573	3.227	1.654	+0.001	−0.013	−0.003	1.639	1.052
C	13	1.6828	2.042	3.826	1.784	0.000	−0.014	−0.003	1.767	1.050
C	14	1.7882	1.778	3.670	1.897	−0.001	−0.015	−0.003	1.878	1.050

[1] 1 centimeter iron wire weighs 0.00194 gm. Hence 1 cm. ≘= 0.0009° rise, the heat capacity of the system being not far from 3800.

[2] 1 cc. NaOH ≘= 0.0122 gm. HNO₃. Hence 1 cc. NaOH ≘= 0.00070° rise.

TABLE II.

BENZOL.

Sample.	No. of Combustion.	Weight of Benzol.	Weight of Sugar.	Initial Temperature.	Final Temperature.	Observed Rise in Temperature.	Thermometer Correction.	Correction for Sugar Burned.	Correction for Iron Burned.	Correction for HNO₃ formed.	Corrected Rise in Temperature.	Per Cent N₂ in Bomb.	Rise in Temp. per gram Benzol.
		gm.	gm.								°	%	
A	12	0.4749	0.2058	1.950	3.445	1.495	+0.001	−0.216	−0.015	−0.004	1.261	4.9	2.655
A	13	0.4054	0.2046	2.893	4.208	1.315	−0.004	−0.215	−0.015	−0.003	1.078	4.9	2.658
A	14	0.7319	0.2119	1.697	3.890	2.193	−0.002	−0.222	−0.018	−0.004	1.942	4.9	2.653
A	15	0.7036	0.2879	2.000	4.192	2.192	−0.001	−0.302	−0.015	−0.005	1.869	4.9	2.656
B	16	0.5493	0.2016	1.110	2.796	1.686	−0.001	−0.212	−0.013	−0.004	1.456	4.9	2.651
B	17	0.5561	0.2017	2.150	3.860	1.710	−0.001	−0.212	−0.014	−0.003	1.480	2.7	2.661
B	18	0.7265	0.2053	1.649	3.818	2.169	−0.001	−0.216	−0.013	−0.004	1.935	2.7	2.663
B	19	0.5972	0.2042	1.238	3.058	1.820	+0.001	−0.214	−0.015	−0.004	1.587	4.9	2.657
B	20	0.5284	0.2025	2.700	4.338	1.638	−0.003	−0.213	−0.014	−0.004	1.404	4.9	2.057
B	21	0.6048	0.2015	3.070	4.907	1.837	−0.003	−0.212	−0.015	−0.004	1.603	4.9	2.650
B	22	0.5846	0.2072	2.089	3.880	1.791	−0.001	−0.217	−0.013	−0.003	1.557	2.7	2.663
A	23	0.5840	0.2073	2.330	4.118	1.788	−0.002	−0.218	−0.010	−0.003	1.555	2.7	2.662
A	24	0.0000	0.2034	1.042	2.860	1.818	−0.001	−0.214	−0.014	−0.003	1.586	10.1	2.643
B	25	0.5315	0.2015	1.139	2.776	1.637	−0.001	−0.212	−0.011	−0.005	1.408	9.6	2.649
A	26	0.5420	0.2051	1.910	3.586	1.676	+0.001	−0.215	−0.015	−0.005	1.442	9.7	2.660
B	27	0.6833	0.2065	1.657	3.708	2.051	−0.001	−0.217	−0.015	−0.007	1.811	11.9	2.650
A	28	0.5536	0.2052	1.955	3.661	1.706	0.000	−0.215	−0.015	−0.003	1.473	3.2	2.661